

3 RADIATION DEFECT AND IMPURITY ATOM INTERACTION
IN PROTON BOMBARDED SILICON

By James B. Robertson and Robert K. Franks

NASA Langley Research Center
Langley Station, Hampton, Va.

and

T. E. Gilmer, Jr.

Virginia Polytechnic Institute
Blacksburg, Virginia

Presented at the Meeting of the American Physical Society

GPO PRICE \$ _____

CFSTI PRICE(S) \$ _____

Hard copy (HC) _____

Microfiche (MF) _____

ff 653 July 65

Seattle, Washington
August 31 - September 2, 1967

FACILITY FORM 602

N 68-26563
(ACCESSION NUMBER)

12
(PAGES)

NASA-TM-60273
(NASA CR OR TMX OR AD NUMBER)

(THRU)

1
(CODE)

26
(CATEGORY)

RADIATION DEFECT AND IMPURITY ATOM INTERACTION
IN PROTON BOMBARDED SILICON

By James B. Robertson and Robert K. Franks*

NASA Langley Research Center

and

T. E. Gilmer, Jr.

Virginia Polytechnic Institute

The majority of the research work done thus far in radiation damage to semiconductors has been done with doped semiconductors. Many of the more recent results show that the effect of radiation on silicon is dependent upon the type and concentration of chemical impurities present in the crystal. Also, mounting evidence has been reported (refs. 1, 2, and 3) that indicates that isolated vacancies and interstitials produced in silicon by irradiation do not remain in the crystal at room temperature or even at liquid nitrogen temperature. It appears that for vacancies or interstitials to remain in silicon, they must associate with chemical impurities, dislocations or with each other.

This paper reports the results of a study of proton bombardment of silicon which gives evidence of an association between vacancies and aluminum atoms within the silicon.

The silicon used in the study was float zone single-crystal silicon with the major active impurity being boron with a concentration of less than 10^{13} atoms/cc. Original resistivity was 3,000 to 4,000 ohm-cm p-type. The crystals were 1-inch-diameter disks, 1.5 to 4.0 mm thick, with faces polished

*Present address: Dept. of Physics, Southern Methodist University,
Dallas, Texas.

for infrared transmission. The crystals were irradiated with 22 MeV protons from the 86-inch cyclotron at Oak Ridge, Tennessee. Two different sample probes were used. The crystals which were mounted on the "hot" probe reached a temperature of 760° C to 870° C due to heating by the proton beam. The temperature of the crystals mounted on the "cold" probe were water cooled and remained below 90° C during bombardment.

All of the crystals which were irradiated on the hot probe showed an increase in p-type conductivity and had a series of infrared absorptions with the main peak at 21.1 microns (fig. 1). These absorptions were observed only with the crystal at liquid helium temperature. The resistivity of the crystals was measured at points along the diameter of both faces with a four-point probe. Figure 2 is the resistivity profile of a crystal whose thickness was greater than the range of 22 MeV protons in silicon. Figure 3 is the resistivity profile of a crystal whose thickness was less than the range of the protons. The acceptors were located only in the regions of the crystals reached by the protons. One of the hot-probe crystals was heated at 600° C for 3 hours; there was no change in the absorption spectrum. Heating the crystal for 2 hours at 1000° C changed the absorption spectrum to that of substitutional aluminum (Al_S).

The crystal irradiated on the cold probe increased in resistivity and showed absorption peaks at 1.8, 3.46, 3.62, 5.5, and 20.5 microns, all of which have been reported previously for irradiated silicon. The 20.5-micron peak had been reported (ref. 4) only for neutron-irradiated silicon. Heating the crystal at 300° C annealed out all of these peaks and new peaks appeared at 8.9 and 14.2 microns. After the crystal was annealed at 600° C, the 8.9- and 14.2-micron absorptions were no longer observable and the spectrum of substitutional aluminum appeared. The experimental results are tabulated in table I.

It was evident that aluminum was being produced in the silicon crystals during proton bombardment. The possibility of the aluminum being diffused into the silicon was eliminated because of the location of the aluminum in the crystal. An activation analysis of an irradiated crystal showed the 1.28 MeV γ from $\text{Al}^{29} \xrightarrow{\gamma, \beta^-} \text{Si}^{29}$ decay. The Al^{29} is most likely produced by a $\text{Si}^{30} (\text{p}, 2\text{p}) \text{Al}^{29}$ reaction. A similar reaction on the more abundant (92.3 percent) Si^{28} would yield the stable Al^{27} isotope. The aluminum concentrations were determined from the absorption coefficients (ref. 5). The production rate of Al^{27} was calculated to be 6×10^{-3} atoms/proton with an accuracy of ± 30 percent.

The absorption center responsible for the 18.9-, 21.1-, and 22.0-micron absorptions which were present in the silicon after irradiation on the hot probe is taken to be a substitutional aluminum atom associated with a lattice defect for the following reasons:

1. The positive identification of Al_S in the cold-probe crystal.
2. The similarity between the new spectrum and that of Al_S .
3. The annealing of the new absorptions into Al_S .

The two spectra are compared in figure 4. The 18.9-, 21.1-, and 22.0-micron absorption lines are higher in energy than their corresponding Al_S lines by 2.6 percent, 0.6 percent, and 2.5 percent, respectively.

Two possible defect distributions were considered: (a) The defects are distributed randomly throughout the crystal and cause a uniform lattice dilation (ref. 6) which could increase the energy of the excited-hole states by decreasing the dielectric constant or by changing the effective mass of the hole. (b) The defects are closely associated with the aluminum atoms and cause individual perturbations of the excited-hole states. The close association model was chosen

because of the difficulty in explaining the difference in energy shifts for the different excited states in terms of a uniform lattice effect. However, if the defects exist only near the Al_S atoms, the radial wave functions of the different excited-hole states could have different amplitudes in the region of the defect so that different perturbations would result. The sharpness of the absorption peaks indicates that the size of the defect and the association are uniform.

The defect is not likely an interstitial silicon atom because we would expect an interstitial to donate a valence electron to fill the hole of the Al_S . The divacancy is ruled out for the same reason; the divacancy being a donor (ref. 7). The possibility that the defect is a single vacancy is unlikely in view of: the high mobility of the vacancy, the stability of the association at $600^\circ C$, and the absence of strong electronic bonding between defect and Al_S atom.

It is believed that the defects are vacancy clusters of fairly uniform size. Pfister (ref. 8) has irradiated silicon at high temperatures and concluded that at $800^\circ C$ to $900^\circ C$, vacancies precipitate to form clusters.

The 8.9-micron and 14.2-micron absorptions which occurred in the cold-probe crystal have not been studied in any detail as yet. It is possible that one or both may be caused by a substitutional and interstitial aluminum pair $(Al_S^- + Al_S^{++})^+$.

REFERENCES

1. Watkins, G. D.; Corbett, J. W.; and Walker, R. M.: Spin Resonance in Electron Irradiated Silicon. *J. Appl. Phys.*, vol. 30, no. 8, Aug. 1959, pp. 1198-1203.
2. Vavilov, V. S.; Vintovkin, S. I.; Lyutovich, A. S.; Plotnikov, A. F.; and Sokolova, A. A.: Radiation Defects in Very Pure Silicon Crystals. *Soviet Phys.-Solid State*, vol. 7, no. 2, Aug. 1965, pp. 399-402.
3. Bemski, G.: Paramagnetic Resonance in Electron Irradiated Silicon. *J. Appl. Phys.*, vol. 30, no. 8, Aug. 1959, pp. 1195-1198.
4. Spitzer, W. G.; and Fan, H. Y.: Effect of Neutron Irradiation on Infrared Absorption in Silicon. *Phys. Rev. (Letters to Ed.)*, Second ser., vol. 109, no. 3, Feb. 1, 1958, pp. 1011-1012.
5. Newman, Rodger: Concentration Effects on the Line Spectra of Bound Holes in Silicon. *Phys. Rev.*, Second ser., vol. 103, no. 1, July 1, 1956, pp. 103-106.
6. Simmons, R. O.; and Balluffi, R. W.: X-Ray and Expansion Effects Produced by Imperfections in Solids: Deuteron-Irradiated Germanium. *J. Appl. Phys.*, vol. 30, no. 8, Aug. 1959, pp. 1249-1258.
7. Watkins, G. D.; and Corbett, J. W.: Defects in Irradiated Silicon: Electron Paramagnetic Resonance of the Divacancy. *Phys. Rev.*, Second ser., vol. 138, no. 2A, Apr. 19, 1965, pp. A543-A555.
8. Pfister, J. C.: Radiation Enhanced Diffusion in Silicon. 7th International Conference on the Physics of Semiconductors. 3 - Radiation Damage in Semiconductors, Academic Press, c.1965, pp. 281-285.

TABLE I.- TREATMENT AND RESULTS FOR SILICON CRYSTALS

Crystal No.	Integrated flux, protons/cm ²	Probe	Annealing temperature, °C	Absorption lines, μ	Minimum resistivity, ohm-cm
1	7.5×10^{15}	Hot	{ Unannealed 600	18.9, 21.1, 22.0 18.9, 21.1, 22.0	----- 330
2	7.5×10^{15}	Hot	{ Unannealed 1000	18.9, 21.1, 22.0 19.4, 21.2, 22.5	60 -----
3	7.5×10^{15}	Hot	Unannealed	18.9, 21.1, 22.0	70
4	57.5×10^{15}	Hot	Unannealed	18.9, 21.1, 22.0	9
5	92×10^{15}	Cold	{ Unannealed 300 600 800 1000	{ 1.8, 5.5, 3.46, 3.62, 20.5 } 8.9, 14.2 19.4, 21.2, 22.5 19.4, 21.2, 22.5 19.4, 21.2, 22.5	~ 30 000 ----- 9 3.5 3.5

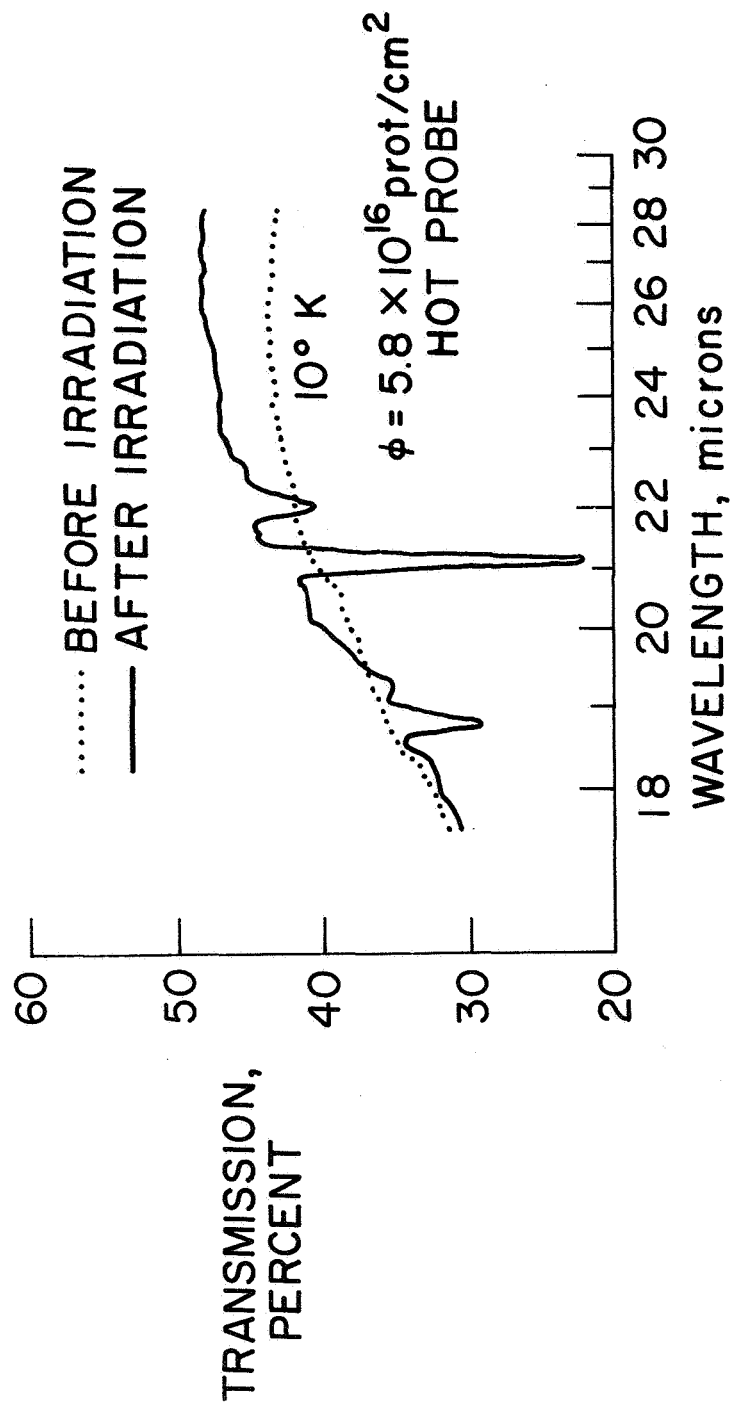


Figure 1.- Absorption spectrum of crystal no. 4.

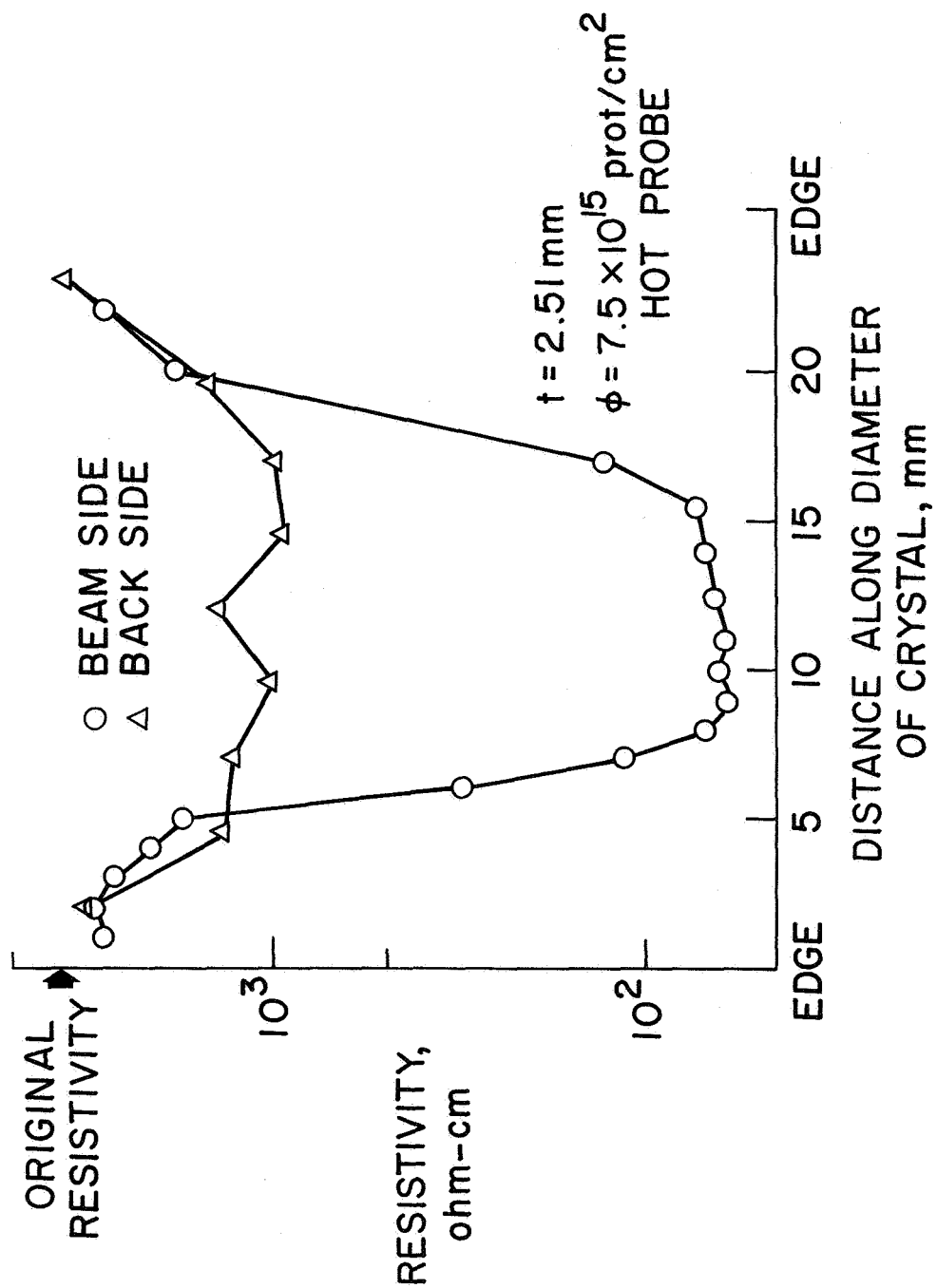


Figure 2.- Resistivity profile of crystal no. 2.

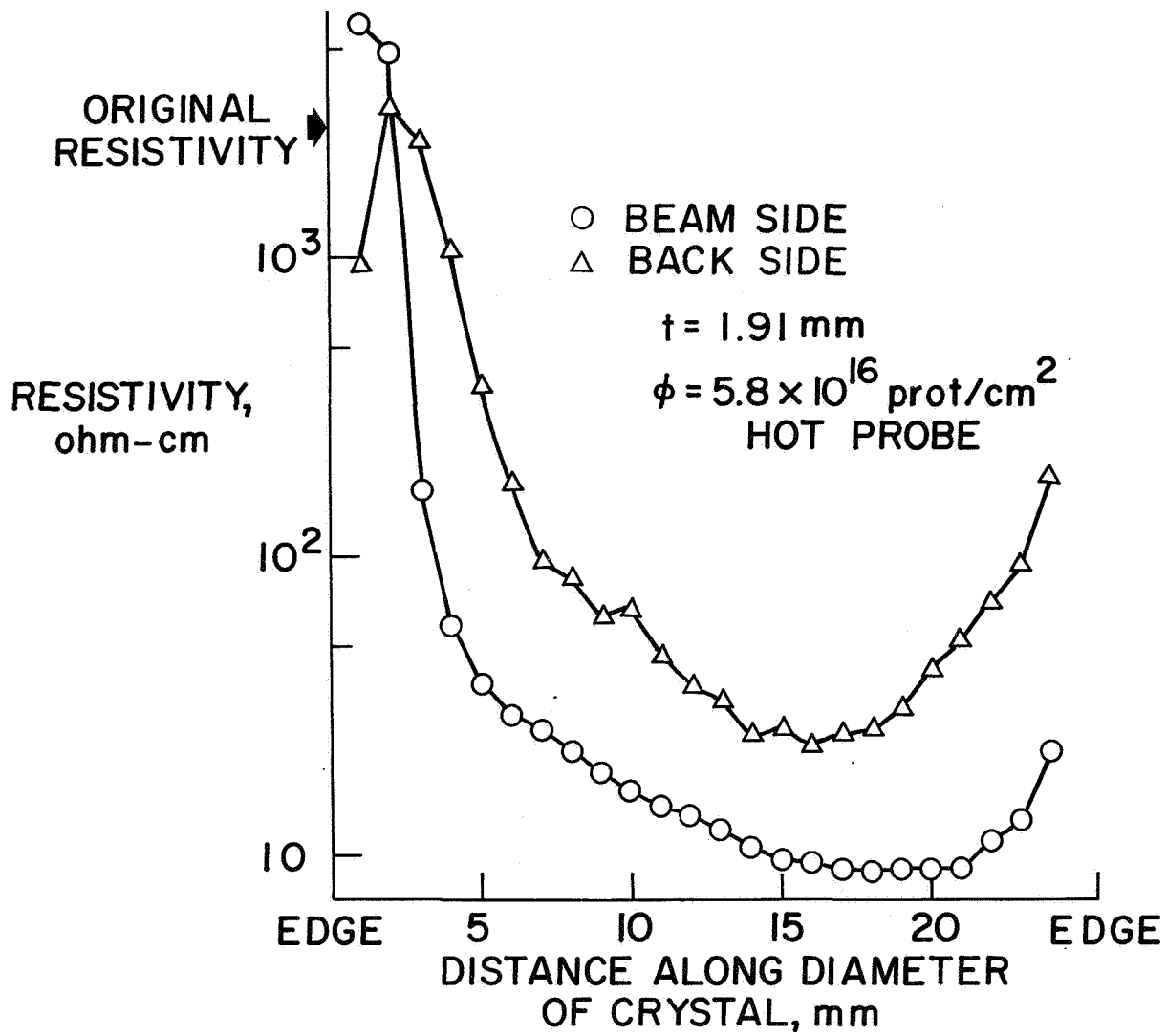


Figure 3.- Resistivity profile of crystal no. 4.

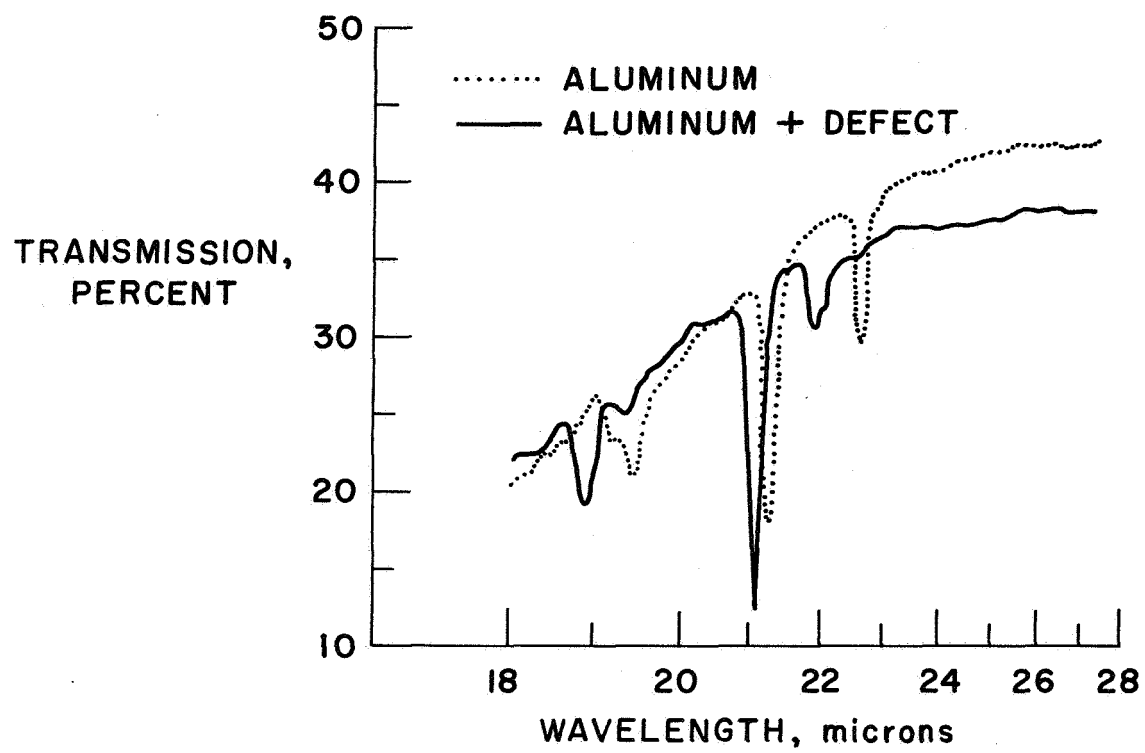


Figure 4.- Comparison of aluminum and defect spectra.